How Multi-Metallic Clusters Grow

Theory and Experiment Combined

Chemists today profit from the steadily growing number of tools and procedures in organic chemistry to build their molecule of choice. The deep understanding of the relation between electronic structure and reactivity as well as mechanisms and stability enable chemists to design more and more complex compounds and simultaneously re-enact the synthesis logically.

Missing links between reactant and product

Systematization in inorganic chemistry, in contrast, is much more complex. Especially in the field of ligand-free clusters, the reaction pathways have still remained a black box to date. The reason for this gap of knowledge originates from a poor structural relationship between reactants and products, and the inability to formulate transition states and intermediate products as the coordinative flexibility of the involved atoms is much higher as in classical organic chemistry.

For a cluster system out of Ta, Ge and As atoms, the formation of multi-metallic clusters was re-traced combining modern inorganic synthesis with state-of-the-art quantum chemistry. For this system, the formation of \([\text{Ta@Ge}_8\text{As}_6]^{3-}\) out of \((\text{Ge}_2\text{As}_2)^{2-}\) was investigated. Although this can only be considered as a small step towards a comprehensive knowledge of inorganic clusters formation, we were able to generalize this model to describe a whole family of multi-metallic clusters.

The apprehension of structural relations and reactivity is not only useful, but essential to design efficient and economical reaction strategies and processes. In organic chemistry, Cory’s concept of retro-synthesis, conceived in the 1980s, is a well-established approach. Big target molecules are disassembled to simple fragments. By utilizing known C-C coupling reactions, a potential route to the target molecule is then constructed. Nevertheless, this concept could not be adopted into inorganic chemistry. The lack of systematic experimental studies toward inorganic cluster formation impeded to derive a general concept.
Especially the formation process of polyatomic complexes and clusters are still a mystery to date. The main reasons are the relatively high flexibility of metal atoms regarding their coordination number and coordination geometry. As a consequence of this flexibility, rapid reorganization of involved molecules widely obliterates the structural relationship between reactant and the final product. Hence intermediate species are normally stripped from analytical assessment.

**Design remains difficult**

In the last decades, mono-disperse metal particles became a high-profile in material science, because they enabled size-controlled synthesis of quantum dots, nano-structured surfaces and solids. Multi-metallic clusters play a special role for chemists as well as physicists in this field: they combine features of mono-dispersed metal particles with opto-electronic and magnetic properties of so called super-atoms. Therefore, multi-metallic clusters can be considered as molecular models of doped metals and catalytically active nano-structures. Designing these clusters is apparently a complex process, as the underlying basic reactions in the solid state, which evolve from interactions of single atoms or molecules, are not understood. That is why the process of cluster formation is of great interest. General comprehension of these “evolutionary” steps in cluster synthesis might be a starting point to control size and shape of metal clusters as well as tuning their physical properties to a specific application.

**Zintl-anions as models**

Newer publications deal with multi-metallic clusters of main group metals and semi-metals which feature an encapsulated transition metal atom – so called endohedral clusters. In the past two decades, a variety of these clusters that differed in sizes and architectures could be obtained. Mostly, they are synthesized in solution from the reaction of homo- and hetero-atomic metal poly-anions (which are named Zintl
anions, see fig. 1) with transition metal compounds. In some cases, the step-wise release of organic ligands from the transition metal compounds was observed, but a conclusion towards the role of the transition metal within the complex reorganization towards the final product was not possible. The lack of knowledge about the relationship between reactant and product becomes evident if considering that all non-deltaedal clusters (e.g. in group 14 metal clusters) are obtained from deltahedral precursors. With a lot of effort, we were able to re-trace the reaction of metal clusters containing Ge, As and Ta atoms within one single reaction, from which a whole series of novel multi-metallic clusters crystallized, which gave us an unparalleled insight into cluster formation.

Synthesizing endohedral clusters

The synthesis of the endohedral clusters start with a 1:1:1 mixture of K, Ge and As. This mixture is filled into a tantalum pipe, which is sealed by arc-welding on both ends and placed into a silica glass ampoule. The latter is sealed in vacuo. In an oven, at 950°C, the intermetallic phase is then formed. Afterwards, the phase is extracted in ethylenediamine using Kryptofix[2.2.2] as cation sequestering agent. After layering the filtered and concentrated solution with toluene, the clusters crystallize as [K(crypt-222)]\(^+\)-salts. The series of obtained clusters comprise a small tetrahedral (Ge\(_2\)As\(_2\))\(^{2-}\) cluster, a 9-atom cage of the composition (Ge\(_7\)As\(_2\))\(^{2-}\) and the endohedral clusters [Ta@Ge\(_8\)As\(_4\)]\(^{3-}\) and [Ta@Ge\(_8\)As\(_6\)]\(^{3-}\). However, only the observation of the intermediate species [Ta@Ge\(_6\)As\(_4\)]\(^{3-}\) allowed for the formulation of a possible reaction pathway. Utilizing recently developed quantum chemical methods to calculate the lowest energy of isomers of multi-metallic systems (GA-RP method) and modeling of the reaction pathway finally served to formulate a reaction cascade for this multi-metallic cluster formation (see fig. 2).

Starting from the tetrahedral (Ge\(_2\)As\(_2\))\(^{2-}\) and an well-known 10-atom cage, (Ge\(_{10}\))\(^{2-}\), that occurs as a by-product under such synthesis conditions, the 9-atom cage (Ge\(_7\)As\(_2\))\(^{2-}\) is formed. This step is observed for homo- as well as multi-metallic clusters that contain group 14 atoms. From this point on, transition metal atoms are integrated, and a partial fragmentation and re-organization is observed. Now, the transition metal atom binds to a cup-shaped cluster shell - imagine a skydiver with his parachute. The transition metal atom is then capable of further reacting with a second tetrahedral cluster to form the intermediate species [Ta@Ge\(_6\)As\(_4\)]\(^{3-}\), in which the Ta atom is encapsulated in the center of the, albeit irregularly shaped, cluster. This species now re-arranges and reacts with another equivalent of the tetrahedral cluster to form the final, highly symmetrical endohedral cluster (see fig. 3).
Hints from the intermediates’ world

Upon a detailed review of the isomers of the crystallized intermediate species, we found a common reaction pathway for all deltahedral, intermetallic clusters containing group 14 atoms. The key species \([\text{Ta@Ge}_6\text{As}_4]^{3-}\) can re-arrange to produce exact fragments of already known non-deltahedral, intermetallic clusters with only small energetic costs. This finding allowed us to align the intermediary species as a common step towards the formation of all known 10, 12, 13 and 14 atom cluster shells of homo- and multi-metallic clusters. In summary, we were able to develop a reaction pathway for the re-organization of deltahedral into non-deltahedral clusters based on our quantum chemical calculations. The isolation of a crystal of the intermediary species was the crucial point to understand the complex rearrangements that take place in this system. Although we were only able to describe one single system, the developed quantum chemical tools provide for an improved basis to illuminate this black box of cluster formation.

Figures 2 and 3 taken from “Understanding of multimetallic cluster growth“, Stefan Mitzinger et al., Nat. Commun., 2016, 7, 10480. DOI:10.1038/ncomms10480.

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